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(54) PHOTOCURABLE OLIGOMER, RESIN COMPOSITION CONTAINING SAME, AND ITS CURED ARTICLE

(57)Abstract:

PURPOSE: To obtain a photocurable oligomer which gives a printing ink excellent in gloss, pigment dispersion, printability, etc., by reacting a specific compd. with rosin.

$$0 - cH_s - 0 - cH_s - 0 - cH_s$$

CONSTITUTION: A photocurable oligomer is prepd. by reacting a compd. of formula I (wherein R is H or CH3) (e.g. a compd. of formula II or III) with rosin. The type of rosin used is determined considering the rate of ultraviolet curing of the resulting ink, the hue of the oligomer, etc., and usually rosins with conjugated double bonds stabilized, such as a hydrogenated rosin or a disproportionated rosin, are suitable. The oligomer can be used for various applications by utilizing its photocurability and gives, when used as a binder, a printing ink excellent in gloss, pigment dispersion, printability, etc.,in comparison with conventional solvent-based printing inks.

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$$0 \longrightarrow CH_{*}-0 - \overset{\text{if}}{C} - \overset{\text{i}}{C} = CH_{*}$$

(— R is H or CH3 among a formula.) — photoresist oligomer which is a reactant with rosin. [Claim 2] The resin constituent characterized by containing photoresist oligomer according to claim 3. [Claim 3] The hardened material of a resin constituent according to claim 2.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001] [Industrial Application] This invention relates to new photoresist ofigomer, the resin constituent using this, and its hardened material. In more detail, it is the ofigomer which has ultraviolet—rays hardenability, and is related with the resin constituent and hardened material using the photoresist ofigomer and this suitable for especially the binder for printing ink. [0002]

[Description of the Prior Art] The ultraviolet curing ink is known as a constituent which blends [Description of the Prior Art] The ultraviolet curing this known as a constituent which blends suitably reactant disents, such as trimethylolpropane triscrylate, a photopolymerization initiator, a pigment, etc. with the partial saturation epoxy resin ester usually reacted and obtained in an epoxy resin and an acrylic acid, and is obtained, in this, although partial saturation epoxy resin ester, unsaturated polyester, etc. are positioned as oligomer in the binder for ink, since this oligomer relates to many ink properties acquired [cure rate / gloss, pigment dispersibility, viscosity, a printability,] closely, it is important also especially in said constituent. [00003]

[0003]
[Problem(s) to be Solved by the Invention] In recent years, even if it is an ultraviolet curing ink, it is required that it should have a printability comparable as conventional solvent mold ink, and it is in the situation that it cannot be satisfied with the partial saturation epoxy resin which is conventional polyfunctional oligomer of this demand enough.
[0004] For example, as a partial saturation epoxy resin, although the reactant of the epoxy resin of bisphenol A and an acrylic acid (meta) is known, when an ultraviolet curing ink is prepared using this, there is a fault that entusflication and the mixting phenomenon of ink are especially accepted notably among printabilities. Therefore, development of the new oligomer which can offer the ultraviolet—rays hardenability ink which has the outstanding printability is demanded. [0005] [0005]

[Means for Solving the Problem] With the conventional technique, this invention is made in order to be able to solve and to solve the inside **** aforementioned technical problem. this invention persons found out that said technical problem could be solved by using the specific oligomer which has a rosin component in a side chain, as a result of repeating research wholeheartedly that the outstanding photoresist oligomer with which can be satisfied of these many engine performance should be developed in consideration of a cure rate besides a printability, stability on board, etc. That is, this invention is a compound [0006] expressed with 1, type (1). [Formula 2]

$$0 \xrightarrow{\text{CH}_{3}-0} -\frac{0}{c} - \frac{1}{c} = \frac{1}{c} = \frac{1}{c} = \frac{1}{c} = \frac{1}{c}$$

[0007] (— they are the inside R and H of a formula, or CH3.) — it is related with the hardened material of the resin constituent characterized by containing the photoresist oligomer and the photoresist oligomer given in 2. 1st term which are a reactant with rosin, and a resin constituent

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acetophenone, 2-hydroxy - Photopolymerization initiators, such as 2-methyl-1-phenyl propane 1-ON, usually among a resin constituent 0.5 - 20 % of the weight. It is desirable to use aliphatic series, aromatic amine or 4, and 4-screw diethylamino benzophenone etc. as an accelerator 0.1 to 10% of the weight among a resin constituent if needed furthermore.

to 10% of the weight among a resin constituent if needed furthermore. [0015] Furthermore, a part of epoxy (meta) acrylate known from the former other than the photoresist oligomer of this invention, urethane (meta) acrylate, etc. can also be used together as a resin constituent of this invention. By adding said reaction diluent etc. further and hypoviscosity-zing it further, etc., the resin constituent of this invention can be used as a coating, adhesives, a solder resist, an overprint varnish, etc., and can also be further used as a charge of moldings lumber. The resin constituent of this invention can be obtained by mixing each component to homogeneity. The hardened material of the resin constituent of this invention can be obtained by invaliding ultraviolet rays or an electron ray with a conventional method and making it harden. od, and making it harden [0016]

[Example] An example explains this invention to a detail further below. The section shows the

weight section among an example. The example 1 colorlessness rosin (product [made from Arakawa Chemical industry], KR-610, disproportionation rosin, acid number 170 (mgKOH/g)) 200 section, the compound 115 section asid formula (2), the methyl triethyl ammoniumchloride 1.14 section, and the METOKINON 0.3 said formula (2), the methyl thethyl ammoniumchloride 1.14 section, and the ME I OKINON 0.3 section are taught, temperature up is carried out to 95 degrees C, and it reacts at 95 degrees C. It reacted until the acid number (mgkOH/g) of reaction mixed liquor became five or less (about 25 hours), and the photoresist oligomer (product A) of this invention was obtained. The obtained product A was light yellow transparence in solid form in ordinary temperature. The result of having measured according to the high-resolution nuclear magnetic resonance (NMR) of the obtained product is shown below.

No. PPM No. PPM 1 166.220 9 124.251 2 166.160 10 124.032 3 146.713 11 77.484 4 145.733 12 No. PPM No. PPM 17 71.707 45 36.872 18 71.682 46 36.741 19 68.352 47 36.695 20 68.181 4 36.555 21 68.04049 36.346 22 67.493 50 36.243 23 67.274 51 35.390 24 67.22552 34.434 25 67.138 53 33.454 26 67.07054 33.338 27 67.028 55 33.092 28 56.260 56 32.808 29 49.999 57 32.61130 47.785 58 32.125 31 47.713 59 32.02132 46.521 60 31.839 33 45.114 61 31.79034 44.224 62 31.738 55 43.661 63 30.80036 40.462 640.724 37 40.379 65 30.555 3838.423 66 29.832 3938.226 67 28.785 40 38.137 68 28.709 41 37.97069 28.635 4237.16770 27.834 43 37.053 given in 3, 2nd term

[0008] The new photoresist oligomer of this invention can be obtained by making the compound and rosin which are expressed with said formula (1) react. As an example of a compound expressed with a formula (1), it is [0009].

$$0 \longrightarrow CH^* - 0 - 0 \\ 0 \\ - CH = CH^* \\ (5)$$

[0010]

******** — things are made. The rosin which was determined in consideration of the et-rays cure rate of the ink obtained, the color tone of photoresist oligomer, etc., and usually carried out stabilizing treatment of the conjugated double bond, such as hydrogenation rosin and disproportionation rosin, is suitable for rosin. For example, the product made from Arakuwa Chemical industry, a trade name, HAIPE-RU (hydrogenation rosin), KR-610 (colorless rosin), etc. can be mentioned.

(0012) The reaction of the compound and rosin which are expressed with a formula (1) perfor preferably about 0.9–1.5Eq of compounds expressed with a formula (1) to 1Eq of the carboxyl group of rosin by the ratio which becomes about 0.95–1.1Eq preferably especially. In order to promote a reaction, it is desirable to use catalysts (for example, triethylamine, benzyl

group of rosin by the ratio which becomes about 0.95—1.1Eq preferably especially. In order to promote a reaction, it is desirable to use catalysts (for example, triethylamine, benzyl dimethylamine, methyl triethyl ammoniumchloride, triphemylphosphine, etc.), and the amount of this catalyst used is 0.3 – 5 % of the weight especially preferably 0.1 to 10% of the weight preferably to reaction raw material mixture. In order to prevent the polymerization under reaction, it is desirable to use polymerization inhibitors (for example, METOKINON, hydroquinone phenothiszin, etc.), and the amount used is 0.05 – 0.5 % of the weight especially preferably to reaction raw material mixture. 60–150 degrees C of reaction temperature are 80–120 degrees C especially preferably for 5 to 60 hours.

10 – 50 hours especially preferably preferably for 5 to 60 hours.

10013 Since hyperviscosity [the resin constituent of this invention / photoresist oligomer 100 weight section to the photoresist oligomer 100 weight section of this invention if needed for the purpose of a viscosity drop. As this reactant dihent, 2-hydroxyethyl (meta) acrylate, Tripropylene glycol difmethlacrylate, hydroxy pivalate neopentyl glycol difmethlacrylate, Bisphenol A tetra-ETOKISHJI (meta) acrylate, trimethylol propane TORIPUROPOKISHITORI (meta) acrylate, Distrimethylol propane TORIPUROPOKISHITORI (meta) acrylate, Distrimethylol propane TORIPUROPOKISHITORI (meta) acrylate, Distrimethylol propane Toric (meta) acrylate, trivicylologenee/fined propane toric on more sorts can be used.

[0014] When using the resin constituent of this invention as printing and a binder for ink.

more sorts can be used.
[0014] When using the resin constituent of this invention as printing and a binder for ink, pigments, such as fast eroticism -, benzidine eroticism -, Lake Red 4R, Lake Red C, brilliant carmine 6B, a copper phthalocyanine blue, a titanium white, and carbon black, can usually be further distributed and used at 50 or less % of the weight among the resin constituent of this invention if needed. Furthermore, extenders, such as an alumina and silicon, may be distributed and used moreover, in case [ike ultraviolet rays] the activity energy line of low energy is comparatively used as a hardening energy line A benzophenone, a thioxan ton, benzoin ethyl ether, 2-methyl-1-[4-(methylthio) phenyl]-2-morpholinopropane-1-ON, A diethoxy

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	No.	PPM
	73	25. 398
	7 4	24.812
	7 5	24. 625
	76	24. 426
	77	23.966
	78	23.902
	79	22.748
	80	21.823
	8 1	21.708
	8 2	21.622
	8 3	21.369
	8 4	21.302
	8 5	19.826
	86	19.774
	8 7	19.594
	88	19.312
	8 9	19.046
	90	18.627
	91	18. 192
	9 2	18.090
	93	16.828
	9 4	16.587
	9 5	14.635
	96	14.522
7	9 7	0

[0018] In addition, the solvent performed the above-mentioned measurement by the proton [0018] In addition, the solvent performed the above-mentioned measurement by the proton decoupling method using heavy chloroform, using a tetramethylisiane as a reference material. [0019] The example 2 colorlessness rosin (product [made from Arakawa Chemical industry], KR-610, disproportionation rosin, acid number 170 (mgKOH/g)) 200 section, the compound 124 section of said formula (3), the triphenyl phosphine 1.16 section, and the METOKINON 0.32 section were taught, it reacted at 95 degrees C (about 25 hours), and the photoresist oligomer (product B) of this invention was obtained. In ordinary temperature, Product B was a solid-state

71 27,131 44 37,014 72 26,08

(product B) of this invention was obtained. In ordinary temperature, Product B was a solid-state and was light yellow transparence.

N. Measurement result of M.R. (0020)

No. PPM No. PPM 1 178.358 20 77.054 2 178.000 21 78.631 3 167.483 22 72.950 4 167.418 23 72.874 5 167.369 24 72.498 6 146.706 25 71.9967145.747 26 71.901 8 137.499 27 71.7339136.358 28 68.428 10136.324 29 68.21511 136.26830 67.596 12134.508 31 67.526 13 127.018 32 67.34214 125.944 33 67.27815 125.613 34 67.210 16 125.473 35 67.13617 124.269 35 56.843 18 124.032 37 56.300 19 77.477 38 58.230 No. PPM No. PPM 39 50.105 66 36.248 40 50.023 67 35.592 41 48.062 6835.390 42 47.789 69 34.437 4347.713 70 33.458 44 48.559 7133.343 45 48.510 72 33.098 46 45.172 7332. 81347 45.074 7432.62148 44.22675 32.270 49 43.673 76 32.188 50 43.845 73 21.12 51 40.482 78 32.036 52 40.374 7931.886 53 38.546 80 31.793 54 38.408 81 30.844 55 38.211 82 30.790 56 38.152 8330.382 57 37.973 84 29.834 5837.150 85 28.821 59 37.059 8628.728 60 37.014 87 28.470 61 36.940 88 27.99962 36.732 89 27.883 63 36.653 90 27.188 64

No.	PPM
93	24. 816
94	24. 715
9 5	24. 634
9 6	24. 636
9 7	23.963
98	22. 775
99	21. 819
100	21. 725
101	21.625
102	21. 373
103	21. 303
104	19. 830
105	19. 597
106	19. 317
107	19. 047
108	18.632
109	18.342
110	18. 253
111	18. 199
112	18. 101
113	17. 832
114	16.845
115	16. 617
116	14.645
117	14. 527
118	0. 337
119	0. 002

36.558 91 26.092 65 36.349 92 25.401

[0021] It kneaded and adjusted using 3 roll mills in the presentation ratio (a numeric value she the weight section.) as shown in application examples 1-5 and example of comparison 1 table 1, and the resin constituent for printing ink was obtained. And the ink performance evaluation of

nce-evaluation approach hardenability (setting time): Stick ***** art [0022] The ink performance-evaluation approach hardenability (setting time). Stick ****** art paper by pressure with RI circuit tester, and find the irradiation time (second) which that ink stops adhering took as the setting time, after carrying out drawdown of the ink 0.6g to carton paper using RI circuit tester (Akira Seisakusho Make) and irradiating ultraviolet rays from the distance of 10cm with 80 W/cm and a high-pressure mercury lamp promptly. Gloss of original ink and emulsification ink: Carry out mecro-scopic observation and evaluate the gloss (original ink gloss) of the print after hardening obtained above.

[0023] Moroover, after draining off water make ink 0.6g and dampening water emulsify with RI circuit tester, drawdown is carried out to carton paper, it hardens on the same conditions as the time of measurement of original ink gloss, the gloss of the printing side after hardening is made into the gloss of emulsification ink, it observes similarly with the naked eye, and the following criteria estimate.

- O: It is very fitness (a printing side is smooth and it is dramatically glossy.).

 O: Fitness (gloss is in a printing side)

 **: Medium [of O and x] x: Defect (there is no gloss in a printing side and reliance does not reflect light in it, either) [0024]

Misting: 1200 revolutions of rolls to which paper was put and ink adhered before the roll of an

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inkometer are carried out, the misting of the ink is carried out, the condition of the ink which dispersed in space is observed with the naked eye, and the following criteria estimate. dispersed in space is observed with O: Few (an activity — suitable) x: Many (an activity — unsuitable)

Detergency: The detergency by the kerosene of the roll of the inkometer to which ink adhe is evaluated.

Bronzing: After carrying out drawdown to carton paper using RI circuit tester and leaving it at a room temperature for 1 hour, on the same conditions as a hardenability trial, ultraviolet rays are irradiated for 0.5 seconds, stiffen them, observe with the naked eye, and the following criteria

O : It compares with the sample which carried out drawdown direct postcure, and is equivalent color tone x. : Separation of a pigment and a vehicle is seen and the reflected light presents gold.

[0025]

[0025] table 1 [] An example The example of a comparison 1 2 3 4 5 1 Two products A 40 30 50 35 45 Product B 5 5 5 KAYARAD R-114 * 1 4036 ** FM-300 *2 29 29 27 T-1420 *3 34 33 TMPTA * 4 19 19 IRUGA cure -907*5 6 66 6 6 6 KAYACURE DETX * 6 1 11 1 111 carmine 6B * 7 2424 2424 24 24 The 24 setting times (second) 0.4 0.3 0.4 0.50.4 0.3 0.3 Hara ink gloss 0 0 0 0 0 0 0 emutaification ink gloss 0 0 0 0 0 0 ** ** misting 0 0 0 0 0 0 x x detergency Good Good Good fitness Good Defact Defact BURON zinc 0 0 0 0 0 x x [0026] Note *1 KAYARAD R-114: Epicost 828 made from onl-ized Shell Epony Acrylic ester ghost. *2 KAYARAD FM-300: — the tetra-ethoxy discrylate of bisphenol A and the Nippon Kayaku Co., Ltd. make — *3 KAYARAD TMPTA: trimethylolpropanetrizacrylate Nippon Kayaku Co., Ltd. make — *4 KAYARAD TMPTA: trimethylolpropanetrizacrylate and the Nippon Kayaku Co., Ltd. make — *5 IRUGA cure -907: The Cibar-Geigy make and photopolymerization initiator. *7 Carmine 6B: the charge of an azo system rosy face.
[0027] The resin constituent of this invention is excellent in gloss and printabilities (a misting, detergency, bronzing, etc.) so that clearly from a table.
[0028]
[Effect of the Invention] The photoresist oligomer of this invention has the advantage which was

[UUZ8]
[Effect of the Invention] The photoresist oligomer of this invention has the advantage which was ascellent in points, such as gloss of the obtained printing ink, pigment dispersibility, and a printability, as compared with conventional solvent mold printing ink, when it is applicable to a wide range application and is especially used as a binder for printing ink by using the photoresist.

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